

Selective vapor phase synthesis of 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine over Al–MCM-41 molecular sieves[☆]

Ajjarapu Ratnamala, Kannekanti Lalitha, Jakkidi Krishna Reddy,
Valluri Durga Kumari*, Machiraju Subrahmanyam

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

Received 13 June 2007; received in revised form 2 October 2007; accepted 3 October 2007

Available online 9 October 2007

Abstract

Cyclization of cyclohexanone, formamide and ammonia in vapor phase gives 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine (AOHA) over zeolites HY, HZSM-5, H β and mesoporous Al–MCM-41 molecular sieves. The screening of catalysts clearly shows that Al–MCM-41 is more suitable for the vapor phase synthesis of AOHA. Correlation of activity and selectivity of metal ion-modified Al–MCM-41 with the NH₃-TPD profiles shows that though the conversions are high, the formation of AOHA is governed by the acid site strength formed by the metal ion used. Interestingly Co²⁺ ion modification of Al–MCM-41 resulted into two sets of acid sites with T_{\max} around 218 °C (weak–medium) and 673 °C (strong). The typical acidity available on Co–Al–MCM-41 around 300–350 °C is showing 100% cyclization activity facilitating the maximum synthesis of AOHA. Based on the product distribution a plausible reaction mechanism is proposed.

© 2007 Published by Elsevier B.V.

Keywords: Cyclization; Cyclohexanone; Al–MCM-41; Amino octahydroacridine

1. Introduction

Zeolites have been extensively used for various acid-catalyzed reactions. However, restrictions imposed by its pore dimensions do not allow to obtain bulkier organic molecules. The discovery of M41S family has opened new windows in materials science. The past decade has witnessed a dramatic increase in the design, synthesis and property evaluation of mesoporous molecular sieves for catalysis, adsorption and separation of bulkier organic molecules and in the production of fine chemicals [1–3].

Tacrine (1,2,3,4-tetrahydro-9-aminoacridine (THA)) is a potent centrally active, reversible acetylcholine esterase inhibitor [4] and it was the first drug licenced for the treatment of mild to moderate Alzheimer's disease. It is used clinically for the treatment of intractable pain of terminal carcinoma [5], myasthenia gravis [6] and as a decurarizing agent [7]. The drug

has also been used as a specific therapy for reversing the signs and symptoms of central anticholinergic syndrome [8] especially with Alzheimer's disease [9,10].

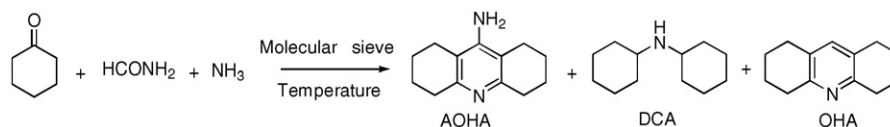
1,2,3,4,5,6,7,8-Octahydro acridin 9-ylamine (AOHA) an intermediate for the synthesis of tacrine is normally prepared conventionally by a modified Von Niementoski reaction [11] of methyl anthranilate and cyclohexanone which gives only 50% yields of 1,2,3,4-tetrahydroacridone which on further chlorination gives 9-chloro 1,2,3,4-tetrahydroacridone. This on further reaction with *p*-cresol and ammonia at 180 °C gives tacrine [12] and on dehydrogenation gives 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine. There are several multi-step synthesis procedures for the synthesis of analogues of tacrine [13].

All the methods reported so far have several drawbacks such as use of hazardous chemicals, expensive or toxic feeds and enormous waste production, etc. Vapor phase synthesis using heterogeneous catalysts is gaining importance due to several advantages in comparison to homogenous catalysis highlighting continuous production, simplified product recovery, catalyst regenerability, etc. Herein, we report a novel synthesis of 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine an intermediate for the synthesis of tacrine in a single step from cheaper raw mate-

[☆] IICT Communication No.: 270531.

* Corresponding author. Tel.: +91 40 27193165; fax: +91 40 27160921.

E-mail address: durgakumari@iict.res.in (V.D. Kumari).



Scheme 1. Cyclization of cyclohexanone, formamide and ammonia over molecular sieve catalysts.

rials like cyclohexanone, formamide and ammonia over zeolites and mesoporous molecular sieves as shown in Scheme 1.

2. Experimental

2.1. Preparation of catalysts

HY (Si/Al=2.6) zeolite was obtained from PQ Corporation, USA. The Conteka, Sweden supplied the HZSM-5 (Si/Al=15) zeolite. H β (Si/Al=10) was obtained from Sud-Chemie, India. Al-MCM-41 (Si/Al=15.5) was synthesized in the laboratory as described earlier [14]. An aqueous solution of aluminum isopropoxide (0.76 g) and sodium hydroxide was added in a 50 ml beaker and stirred while heating till a clear solution appeared. Then 9.4 ml of tetra ethyl ammonium hydroxide (TEAOH) was added to the solution while cooling under stirring (Solution-A). Simultaneously the required amount of tetraethylorthosilicate was taken in another beaker in 50 ml water (Solution-B) and then Solution-A was added slowly to Solution-B with stirring. After stirring for 2 h, hexadecyltrimethyl ammonium bromide (HDTAB) 10.55 g was added slowly to the above mixture. Finally, the gel mixture having the molar composition of 31 SiO₂:Al₂O₃:2.2 HDTAB:3.16 TEAOH:1.89 Na₂O:615 H₂O was transferred into an autoclave and heated at 100 °C for 24 h with an auto-generated pressure observed to be around 60 psi. The recovered product was calcined at 500 °C in air for 12 h to expel the imprisoned template.

The Al-MCM-41 is modified by metal ions like V (V), Fe (III), Co (II), Cu (II), La (III) and Ce (III) during synthesis to incorporate metal ions in the framework. Corresponding nitrate or acetate salts of the metals are taken as precursors. The Si/M=100 is maintained in all the M-Al-MCM-41 catalysts. The method of preparation is similar to that of Al-MCM-41 except that the metal precursor is dissolved in NaOH and aluminum isopropoxide solution before adding TEAOH. All the

catalysts were characterized by various techniques like XRD, BET surface area, NH₃-TPD and UV-vis DRS techniques.

2.2. Characterization

The diffraction patterns of the Al-MCM-41 and modified Al-MCM-41 catalysts were recorded with Siemens D-5000 X-ray diffractometer using Cu K α radiation. BET surface areas were measured in all glass high-vacuum system by N₂ adsorption at -196 °C. UV-vis diffuse reflectance spectroscopy with a sphere reflectance spectroscopy measurements were recorded on Cintra 10_e spectrometer using pellets of 50 mg sample ground with 2.5 g of KBr. TEM was carried out on Technai F12 Phillips unit operated at 80 kV with filament current of 27 mA. Pore properties of MCM-41 obtained using NOVA 1200 e YUASA surface area and pore size analyzer and are given as supplementary information. The pore size of MCM-41 as synthesized is around 20 Å. The pore size of metal-modified Al-MCM-41 is expected to be lower than this value due to the metal incorporation in frame as well as in the outer wall of the mesopore which is also supported by the decrease in the surface area of these systems as shown in Table 1. Temperature-programmed desorption studies were also conducted on Auto Chem 2910 (Micromeritics, USA) instrument. In a typical experiment for TPD studies about 200 mg of oven-dried sample (dried at 120 °C for over night) was taken in a U-shaped quartz sample tube. Prior to TPD studies, the catalyst was pretreated at 200 °C for 1 h by passing pure helium (99.99%, 50 ml/min). After pretreatment of the sample, it was saturated with anhydrous ammonia in a flow of 10% NH₃-90% He mixture at 80 °C with a flow rate of 75 ml/min and was subsequently flushed at 100 °C for 2 h to remove physisorbed ammonia. TPD analysis was carried out from ambient temperature to 750 °C at a heating rate of 10 °C/min. The amount of ammonia desorbed was calculated using GRAMS/32 software. TEM analysis was carried out on TECHNAI F12 Philips unit with filament current of 27 mA.

Table 1
Physical characteristics of metal-modified Al-MCM-41 catalysts

Catalyst	Metal wt% (g)	<i>d</i> -Spacing (Å)	Unit cell parameter <i>a</i> ₀ (Å)	BET surface area (m ² /g)	TPD of ammonia (<i>T</i> _{max} , °C)		Total acidity (mmol/g)
					LT peak	HT peak	
Al-MCM-41		41.326	47.72	894.0	0.256 (307)	0.164 (444)	0.3203
V-Al-MCM-41	0.585	39.74	45.88	840.5	0.289 (290)	0.065 (372)	0.354
Fe-Al-MCM-41	0.642	37.34	43.11	828.0	0.316 (307)	0.169 (444)	0.485
Co-Al-MCM-41	1.35	44.17	51.00	800.0	0.230 (218)	0.218 (673)	0.448
Cu-Al-MCM-41	0.73	38.55	44.51	825.0	0.243 (300)	0.187 (426)	0.429
La-Al-MCM-41	1.59	43.11	49.78	833.0	–	–	–
Ce-Al-MCM-41	1.61	48.72	56.25	746.0	0.235 (311)	0.234 (395)	0.469

Si/M=100, Si/Co=50, *a*₀=2*d*₁₀₀/√3.

Table 2
Synthesis of 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine over molecular sieve catalyst

Catalyst (Si/Al ratio)	% cyclohexanone conversion	% selectivity				Total acidity (mmol/g)
		DCA	OHA	AOHA	Others	
HY (2.6)	96	23.35	9.98	23.32	43.35	0.709
HZSM-5 (15)	78	3.84	2.88	20.83	72.45	0.530
H β (10)	84	34.98	54.85	14.02	–	0.527
Al-MCM-41 (15.5)	91	29.96	16.61	43.97	9.46	0.320

Feed = cyclohexanone:formamide:ammonia = 2:1:3, temperature = 350 °C, WHSV = 1, DCA = dicyclohexyl amine, OHA = octahydroacridine, AOHA = 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine.

Table 3
Effect of metal modification on cyclization reaction

Metal	% conversion	% selectivity			
		DCA	OHA	AOHA	Others
Al-MCM-41	91	29.96	16.61	43.97	9.46
Cu-Al-M-41	97	28.49	15.40	48.85	7.26
V-Al-M-41	100	25.05	12.15	62.78	0.0
La-Al-M-41	92	28.92	16.43	50.75	3.90
Fe-Al-M-41	95	35.24	7.55	52.64	4.57
Co-Al-M-41	92	21.29	6.99	67.0	4.72
Ce-Al-M-41	98	24.38	14.89	53.84	6.89

Feed = cyclohexanone:formamide:ammonia = 2:1:3, temperature = 350 °C, WHSV = 0.5, DCA = dicyclohexyl amine, OHA = octahydroacridine, AOHA = 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine.

2.3. Catalytic activity

The reactions were carried out using a tubular down flow Pyrex reactor of 55 cm in length and 20 mm diameter. All the reactions were carried out in the temperature range of 250–350 °C. The reaction mixture was fed from the top using a syringe pump (B. Brawn, Germany). The product stream was collected through a condenser using ice-cooled water circulation down the reactor. The products were analyzed by gas chromatography using 10% SE-30 column. The samples collected at 2nd hour were analyzed and the product distribution is reported in Tables 2 and 3. The analysis was confirmed by Agilent 6890GC with 5973N mass selective detector, HP-5 MS column and He as a carrier gas.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD patterns of Al-MCM-41 and metal-modified Al-MCM-41 are shown in Fig. 1. The XRD patterns of Al-MCM-41 and metal-modified Al-MCM-41 show a strong peak in the 2θ range of 1.5–2.6 due to 100 reflection line and small peaks due to higher order 110, 200 and 210 reflections indicating well-ordered mesoporosity of the materials. The XRD patterns obtained are in good agreement with the previous reports [15]. Further the appearance of above peaks in the metal-modified Al-MCM-41 catalysts suggests that the hexagonal array of mesopores in MCM-41 is retained after the

incorporation of metals. However the intensities of these peaks decrease with the metal ion incorporation and the extent depends on the amount of metal ion used. Greater the Si/M ratio greater the integrity. Thus increase in metal ion concentration increases d -values and unit cell parameter. These are also seen increasing when metal ions of large size are used compared to that of Si^{4+} . A loss in the higher order (110, 200, 210 planes) is observed with increasing metal ion incorporation. This can be seen clearly in Fig. 1 insert showing the difference in the crystallinity of Co-Al-MCM-41 (Si/M = 50) and V-Al-MCM-41 (Si/M = 100). The XRD patterns of La-Al-MCM-41 and Ce-Al-MCM-41 also show poor crystallinity in the long range which may be seen due to the large ionic size of these metals. Similar observations were reported by earlier workers with different metal ions incorporated into MCM-41 [16,17]. The values of d -spacing and lattice parameter (a_0) increase only with low Si/M ratio and metal ion of bigger size as shown in Table 1.

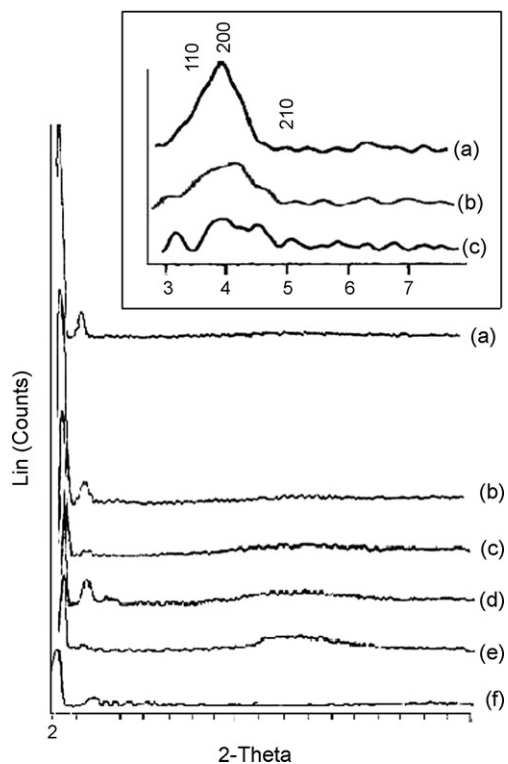


Fig. 1. X-ray diffraction pattern of (a) Al-MCM-41, (b) V-Al-MCM-41, (c) Co-Al-MCM-41, (d) Cu-Al-MCM-41, (e) La-Al-MCM-41 and (f) Ce-Al-MCM-41.

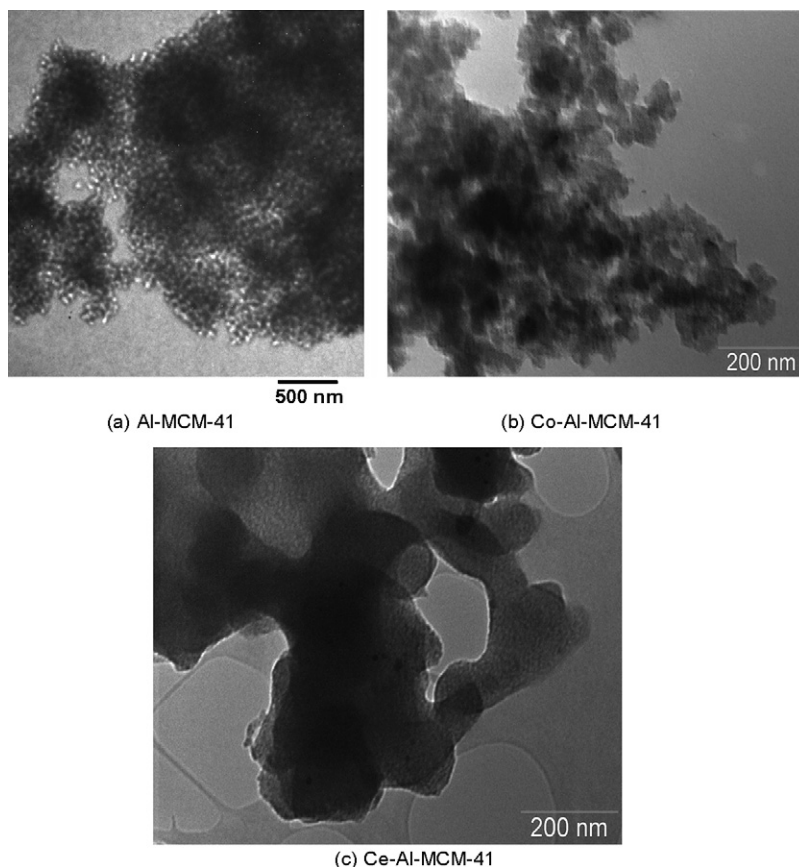


Fig. 2. TEM images of a) Al-MCM-41 b) Co-Al-MCM-41 and c) Ce-Al-MCM-41.

Table 1 shows the physical characteristics of metal-modified Al-MCM-41.

3.1.2. Surface area

The BET surface areas of metal-modified Al-MCM-41 are generally decreased with metal ion modification. It is clear from the literature that metal incorporation in the outer layer of the mesopore may result in decrease in surface area and also the pore size [18]. The Co- (where Si/M ratio is low) and Ce- (where Si/M ratio is high and larger metal ion) modified Al-MCM-41 show maximum decrease in surface area (Table 1).

3.1.3. TEM

The TEM photographs of Al-MCM-41 and metal-modified Al-MCM-41 are shown in Fig. 2. The hexagonal array pattern of Al-MCM-41 is seen well maintained in the metal-modified Al-MCM-41 systems. Thus TEM photographs of metal-modified Al-MCM-41 are supporting characteristics of mesoporous materials.

3.1.4. UV-vis diffuse reflectance spectroscopy

The coordination geometry of the metal-incorporated Al-MCM-41 was studied by the UV-vis diffuse reflectance spectroscopy. The DRS of Al-MCM-41 and Co-Al-MCM-41 catalysts are shown as representative samples of this series in Fig. 3. In pure Al-MCM-41, a strong absorption band at 200 nm in the UV range is assigned to the presence of framework alu-

minum [19]. A strong band is also observed in the case of Co-Al-MCM-41 around 240 nm that may be assigned to low-energy charge transfer between ligands and central Co^{2+} in tetrahedral symmetry [20,21]. Weak but distinctive triplet of $d-d$ transitions

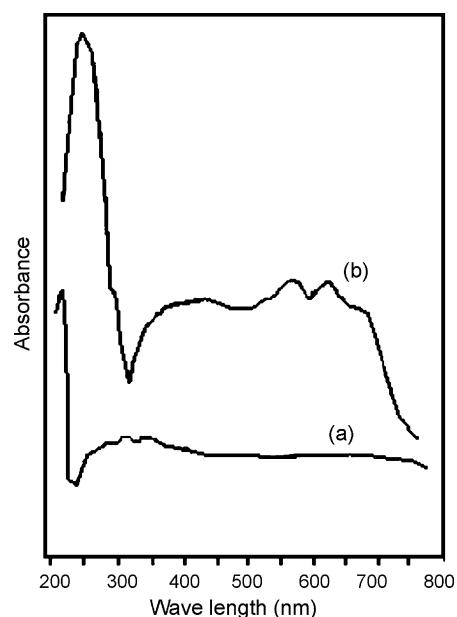


Fig. 3. UV-vis diffuse reflectance spectra of (a) Al-MCM-41 and (b) Co-Al-MCM-41.

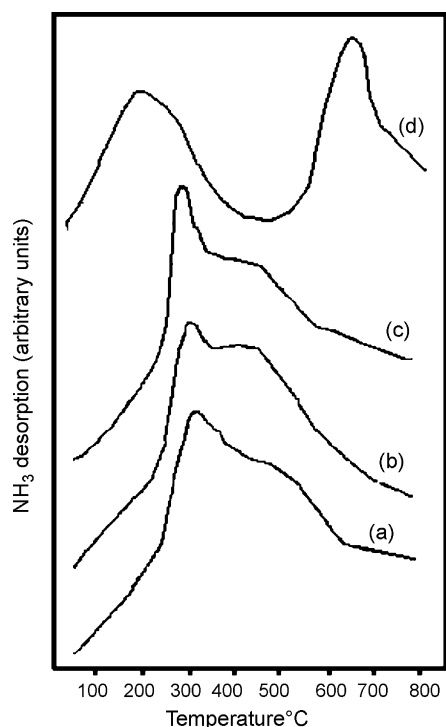


Fig. 4. NH_3 -TPD profiles of Al-MCM-41 (a) bare and metal-modified, (b) Ce, (c) V and (d) Co.

in the range of 500–700 nm with peak maxima around 530, 625 and 680 nm are observed due to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ transitions of Co^{2+} [22,23]. All these results show that majority of the cobalt ions are occupied in the framework positions and the availability of these sites are responsible for maximum cyclization activity.

3.1.5. NH_3 -TPD measurements

In general, all metal-modified Al-MCM-41 show an increase in total acidity. This increase is more in the case of Fe- and Ce-modified Al-MCM-41. The characteristic TPD profiles of bare and metal-modified Al-MCM-41 are shown in Fig. 4. In case of Al-MCM-41 a sharp low-temperature (LT) peak and a broad high-temperature (HT) peak as a shoulder associated with LT peak are seen. The TPD profiles did not show much variation and T_{max} of LT peak (290–311 °C) and HT peaks (372–466 °C) are more or less in the same range in metal-modified Al-MCM-41. However, an interesting feature is observed in the case of Co-Al-MCM-41 wherein the characteristic unresolved TPD profile of Al-MCM-41 is seen distinctly resolved into a low-temperature and a high-temperature peak, shifting the T_{max} of LT peak to 218 °C and T_{max} of HT peak to 673 °C showing the clear-cut separation of weak-medium and strong acid sites in Co-Al-MCM-41.

3.2. Catalytic activity

Initial screening of the catalysts was carried out over HY, HZSM-5, H β and Al-MCM-41 at 350 °C with WHSV (weight hourly space velocity) of 1 and the results are shown in Table 2. The stoichiometric feed molar ratio of 2:1:3

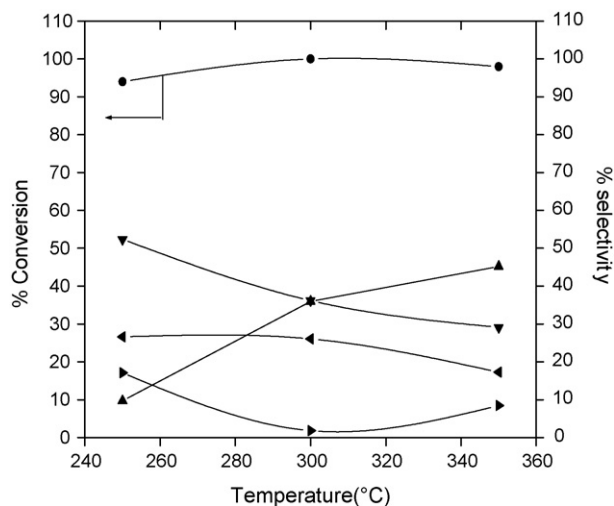


Fig. 5. Effect of temperature on cyclization reaction (●) cyclohexanone conversion and selectivity of (▲) AOHA, (▼) DCA, (◄) OHA and (►) others.

of cyclohexanone, formamide and ammonia was maintained in all the experiments. The cyclization reaction is forming 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine (AOHA), dicyclohexylamine (DCA) and octahydroacridine (OHA) as major products along with other side products. The catalytic activity in terms of cyclohexanone conversion follows in the order of Al-MCM-41 ~ HY > H β > HZSM-5. The selectivity of AOHA is also more with mesoporous Al-MCM-41 compared to large pore HY, H β and medium pore HZSM-5. Though the conversions are high on all the zeolites studied, increase in AOHA selectivity with increase in pore size may be seen as due to the easy diffusion of the reactants and products in and out of the pores of the catalyst without any constraints. However, the differences observed in product distribution are not governed by pore size alone but also by the relative number of acid sites available at reaction temperatures studied. The presence of unsuitable acid sites may be allowing the reactants to participate in side reactions diverting the mechanistic pathway of the main reaction. Thus high cyclohexanone conversion and selectivity for AOHA over Al-MCM-41 with minimum by-products (total acidity 0.32 mmol/g) indicates the presence of suitable acid sites favoring the reaction. To fine-tune the formation of the desired product AOHA, it is aimed to modify the Al-MCM-41 by metals to obtain acid sites of suitable strength. Furthermore, various reaction parameters like effect of temperature, WHSV are optimized.

3.2.1. Effect of temperature

Fig. 5 shows the effect of temperature studied in the range of 250–350 °C over Al-MCM-41 (Si/Al = 15.5). The conversion increased with increase in temperature from 250 to 350 °C and further increase in temperature decreased the activity leading to heavy coking. The selectivity of AOHA is low at lower temperature and conversions increased improving the selectivity at higher temperature (350 °C). Therefore, 350 °C is chosen for studying effect of other parameters on cyclization reaction.

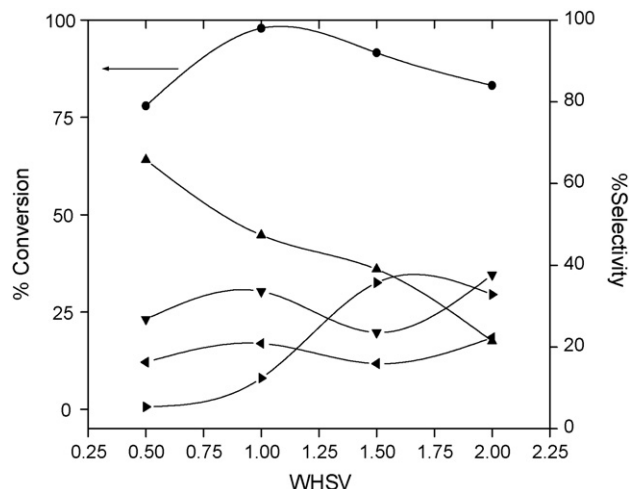


Fig. 6. Effect of WHSV on cyclization reaction (●) cyclohexanone conversion and selectivity of (▲) AOHA, (▼) DCA, (◄) OHA and (►) others.

3.2.2. Effect of WHSV

The effect of WHSV on cyclohexanone conversion and product selectivity was studied by carrying out the cyclization reaction at various space velocities (WHSV = 0.5, 1, 1.5 and 2) at 350 °C and the results are shown in Fig. 6. The cyclohexanone conversion decreases with increase in space velocity from 0.5 to 2.0 h⁻¹. The selectivity of AOHA minimized with decrease in contact time. Thus, high contact time of 0.5 h⁻¹ is desirable for cyclization activity and selectivity. DCA selectivity is maximum at higher contact times indicating the non-availability of formamide for cyclization due to decomposition.

3.2.3. Effect of metal modification

It is well acknowledged that the metal ion modification in zeolites and MCM-41 brings changes in the total acidity, acid site strength and the nature of acid sites. In the present investigation, Al-MCM-41 (15.5) is modified by incorporating metal ions like V⁵⁺, Fe³⁺, Co²⁺, Cu²⁺, La³⁺ and Ce³⁺ during synthesis. Earlier reports on characterization of metal-modified MCM-41 discussed the possible location of these metal ions depending on the method of incorporation [24]. It is concluded that metal ions incorporated during synthesis are stable and the stability of impregnated metal ions is always an issue. In the present investigation, the metal ions are incorporated during the synthesis in order to achieve framework incorporation of the metal ions. The locations of metal ions are characterized by UV–vis DRS and the strength of the acid sites suitable for cyclization are evaluated by TPD of ammonia. Table 1 shows the physical characteristics of metal-modified Al-MCM-41. The cyclization activity of the metal-modified Al-MCM-41 is shown in Table 3. The increase in total acidity in general increased conversion. However, the product distribution varied depending on the nature of metal ions used for modification. Metal ions like V, Co are showing the tendency to form AOHA selectively. The improved selectivity of one metal over the other on modified Al-MCM-41 system may be seen due to difference in acid site strengths that are generated on modification.

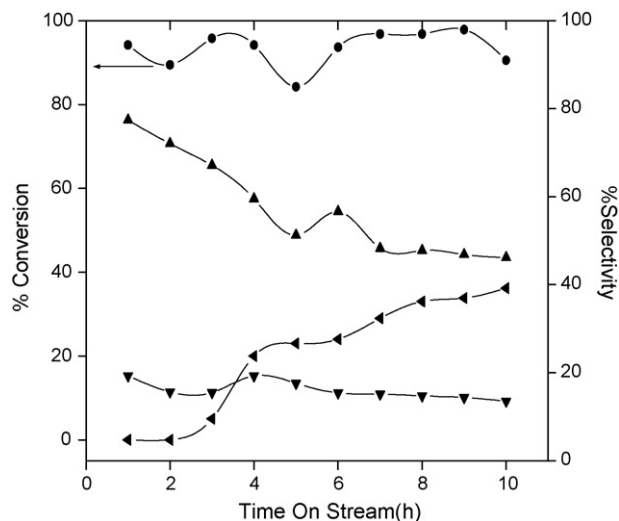
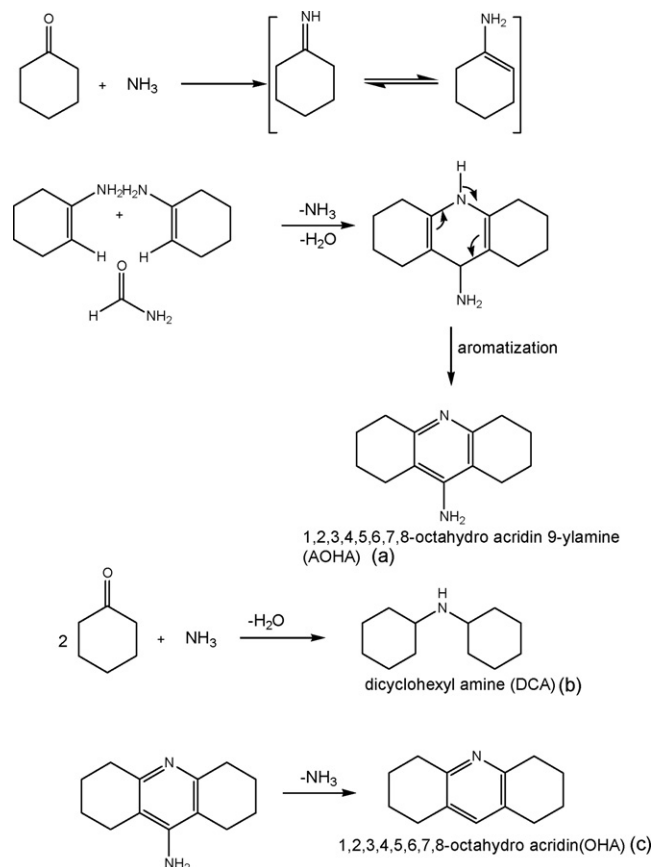


Fig. 7. Effect of time on stream activity of cyclization reaction (●) cyclohexanone conversion and selectivity of (▲) AOHA, (▼) OHA and (◄) others.

In the case of Co-Al-MCM-41, NH₃-TPD profile clearly shows a demarcation of low-temperature (T_{\max} , 218 °C) and high-temperature (T_{\max} , 673 °C) peaks representing two sets of acid site strengths as shown in Fig. 3 and Table 1. The strong acid sites on Co-Al-MCM-41 are available only above 400 °C. The weak-medium acidic sites available in the low-temperature range and improved the selectivity of AOHA to 67%. Thus,



Scheme 2. Plausible reaction mechanism for formation of AOHA.

Co modification on Al–MCM-41 resulted into a typical acidity producing 100% cyclization activity and high selectivity of AOHA.

3.2.4. Time on stream

The cyclization reaction was studied for time on stream activity over Co–Al–MCM-41 at 350 °C at WHSV of 0.5, i.e. at optimized reaction conditions and the results are given in Fig. 7. The cyclohexanone conversion and selectivity of AOHA are high in the first 3 h and slowly decrease with time and level off to 42%. With increase in time deamination is taking place leading to the formation of OHA and accumulation of coke over a period.

3.2.5. Reaction mechanism

Based on the product distribution a plausible reaction mechanism is proposed for the formation of AOHA, DCA and OHA and is shown in Scheme 2. The reactant cyclohexanone first forms imine with ammonia, which isomerises to an amine. When two moles of an imine–amine intermediate on cyclization with formamide, and further deamination and dehydrogenation forms the major product (a) 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine and this on deamination produces a by-product (c) octahydroacridine, direct condensation of cyclohexanone in the presence of ammonia forms another by-product (b) dicyclohexylamine.

4. Conclusions

Vapor phase cyclization of cyclohexanone, formamide and ammonia at 350 °C over Co-modified Al–MCM-41 involves the formation of imine ↔ amine intermediates, which on further dehydrogenation and deamination form 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine (AOHA) as major product, DCA and OHA as by-products. Al–MCM-41 with cobalt modification has generated suitable acidity for selective formation of 1,2,3,4,5,6,7,8-octahydro acridin 9-ylamine (AOHA). The observed product distribution justified the mechanistic pathway proposed.

Acknowledgement

A R M is thankful to CSIR, New Delhi, for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.10.002.

References

- [1] A. Ratnamala, M. Subrahmanyam, V. Durga Kumari, Appl. Catal. A: Gen. 264 (2004) 219.
- [2] A. Ratnamala, V. Durga Kumari, M. Subrahmanyam, N. Archana, Chem. Commun. (2004) 2710.
- [3] M.G. Clerici, Top. Catal. 13 (2000) 373.
- [4] S. Maayani, H. Weinstein, N. Ben-Zui, S. Cohen, M. Sokolovsky, Biochem. Pharmacol. 23 (1974) 1263.
- [5] V. Stone, W. Moon, F.H. Shaw, Br. Med. J. 1 (1961) 471.
- [6] C.R. Jones, M. Davis, Med. J. Aust. 2 (1975) 650.
- [7] S. Gershon, F.H. Shaw, J. Pharm. Pharmacol. 10 (1958) 638.
- [8] W.K. Summers, K.R. Kaufman, F. Altman Jr., J.M. Fischer, Clin. Toxicol. 16 (1980) 269.
- [9] K.L. Davis, R.C. Mohs, J.R. Tinklenberg, N. Engl. J. Med. 301 (1979) 946.
- [10] A. Albert, W. Gledhill, J. Soc. Chem. Ind. 64 (1945) 169.
- [11] V. Petrow, J. Chem. Soc. (1947) 634.
- [12] P.R. Carlier, Y.F. Han, E.S.-H. Chow, C.P.-L. Li, H. Wang, T.X. Lieu, H.S. Wang, Y.P. Pang, Bioorg. Med. Chem. 7 (1999) 351.
- [13] W.H. Kaye, N. Sitaram, H. Weingarter, M.H. Eber, S. Smallberg, J.C. Gillin, Biol. Psychiatry 17 (1982) 275.
- [14] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, J.C. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
- [15] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
- [16] W.A. Carvalho, P.B. Varaldo, M. Wallau, U. Schuchardt, Zeolites 18 (1997) 408.
- [17] S.C. Laha, P. Mukherjee, S.R. Sainkar, R. Kumar, J. Catal. 207 (2002) 213.
- [18] A. Ratnamala, V. Durgakumari, K. Lalitha, M. Subrahmanyam, Catal. Commun. 8 (2007) 267.
- [19] M.A. Zanjanichi, Sh. Asgari, Solid State Ionics 171 (2004) 277.
- [20] A. Martinez-Hernandez, G.A. Fuentes, Appl. Catal. B: Environ. 57 (2004) 167.
- [21] Z. Luan, J. Xu, H. He, J. Klinowski, L. Kevan, J. Phys. Chem. 100 (1996) 19595.
- [22] I. Pettiti, S. Colonna, S.D. Rossi, M. Faticanti, G. Minelli, P. Porta, Phys. Chem. Chem. Phys. 6 (2004) 1350.
- [23] W. Fan, R.A. Schoonheydt, B.M. Weckhuysen, Chem. Commun. (2000) 2249.
- [24] A. Tuel, Micropor. Mesopor. Mater. 27 (1999) 151.